Brief Overview to Fuels & Materials Compatibility

Edward W. English, II
Vice President – Technical Director
Fuel Quality Services, Inc.
eenglish@fqsinc.com

OVERVIEW

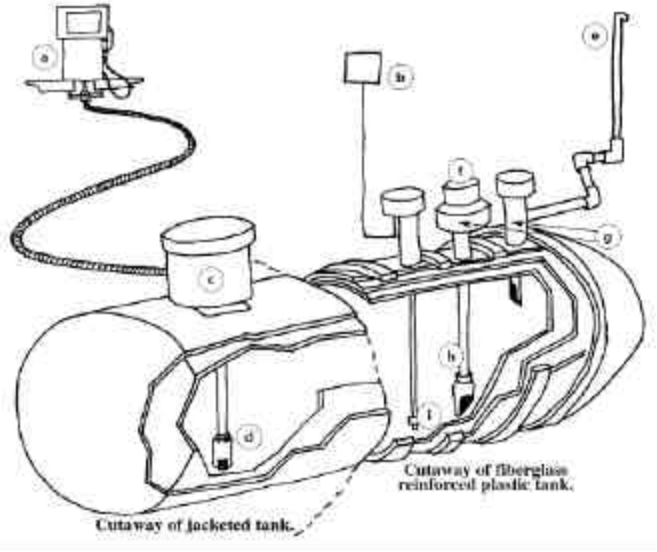
- General Background
- Petroleum Based Fuels
- Biodiesel Blend Fuels
- Ethanol Blend Fuels
- Conclusion

General Background

- UST configuration:
  - Tank & Piping
  - Pump System
  - Dispenser & Nozzle
  - Vapor Recovery System
- External Environment Controls:
  - Corrosion Protection
  - Leak Detection
  - Overfill Protection
  - Spill Protection

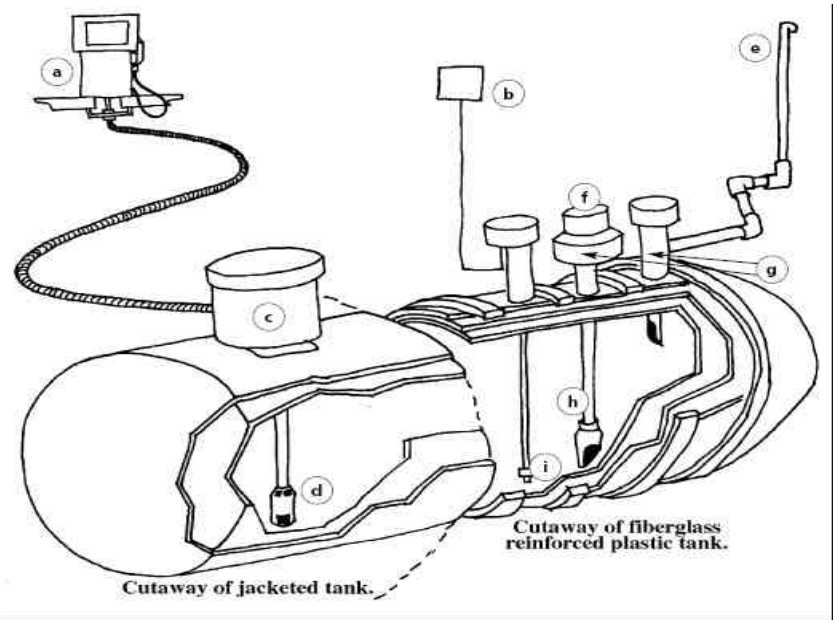
Required by 40 CFR 280

- No Internal Environmental Controls



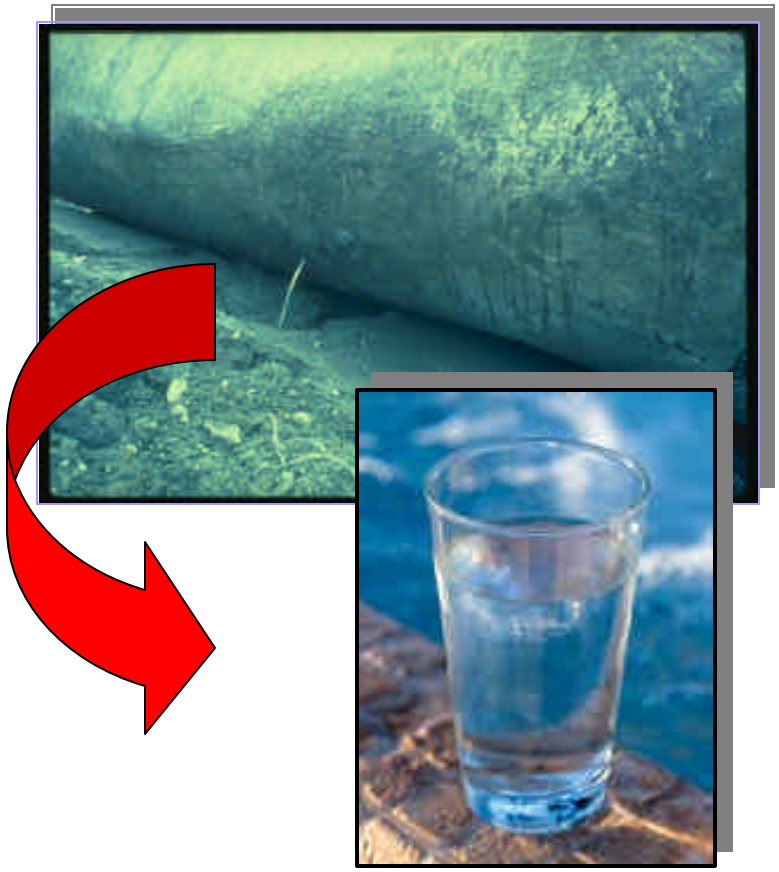
General Background

- Typical materials include
  - Metals
    - aluminum, brass, copper, steel, zinc
  - Non-metals
    - Elastomers - Flexible hoses, seals gaskets and packing,
    - Thermoplastics - Underground flex piping, sumps and vapor recovery tubing,
    - Thermosets - Rigid piping and USTs,
    - Ceramics, pipe dope, and organic coatings



General Background

- Release of product from underground storage tanks (UST) poses a significant threat to the environment and human health by contamination of local ground water.
  - 1977, Provincetown Massachusetts
  - 1980, Glenwood Colorado
  - 1983, Dover-Walpole Massachusetts



General Background

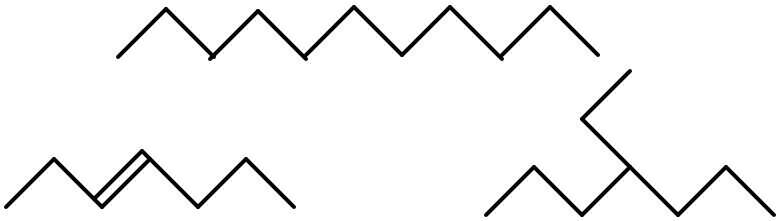
- Product types for USTs
  - Petroleum based fuels
  - Biomass based fuels

General Background

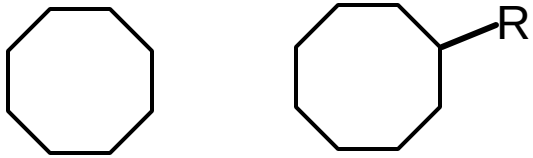
- Petroleum based fuels
  - Aviation
  - Diesels
  - Jet
  - Motor Gasolines

General Background

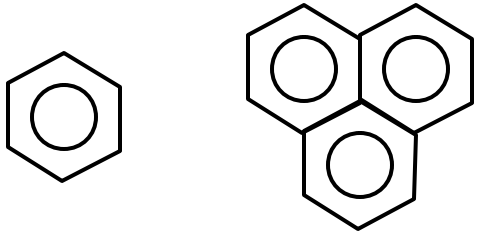
- Simple Structures In Petroleum Fuels:
  - Linear & branched hydrocarbons



  - Cyclic



  - Aromatic & Polyaromatic

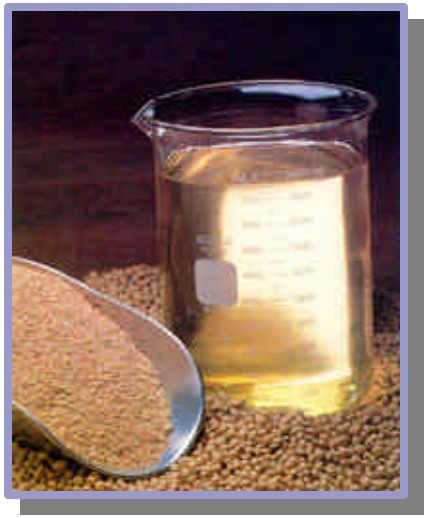


General Background

- In general petroleum based fuels are:
  - Considered benign, electrically non-conductive and non-corrosive,
  - do not absorb into or permeate through metals,
  - typically not observed to significantly swell or permeate [thermoset] fiberglass tanks, rigid piping, and sumps
  - Have been observed to swell and permeate some thermoplastic and elastomeric materials,

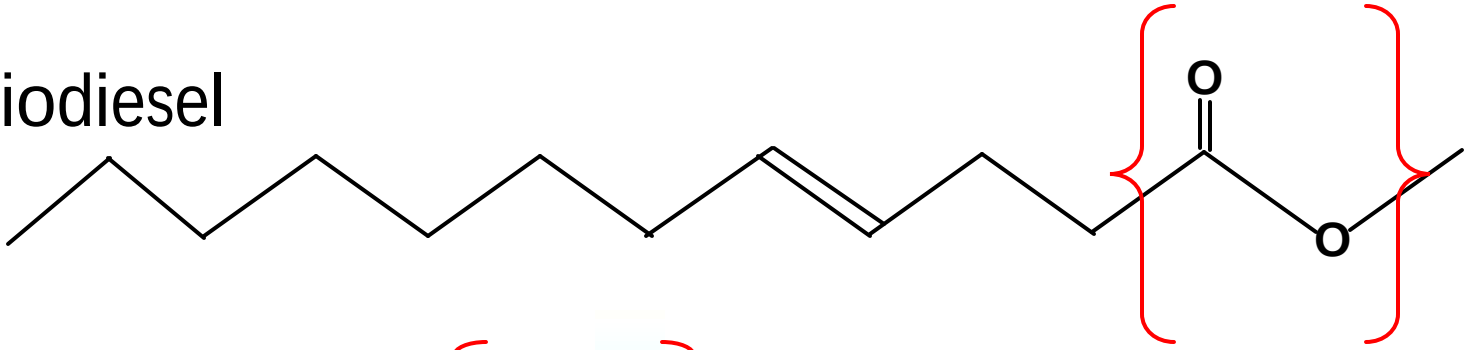
General Background

- Biomass Fuels:
  - Biodiesel
    - B100
    - B20
  - Ethanol
    - E10
    - E85

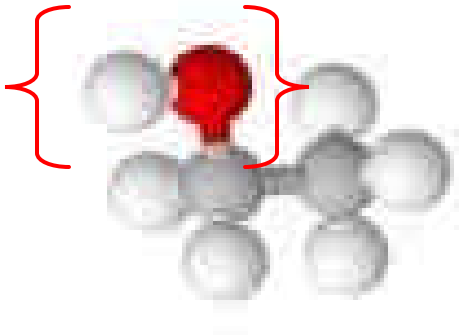


General Background

- Simple Structures In Biomass Fuels:
  - Biodiesel



  - Ethanol



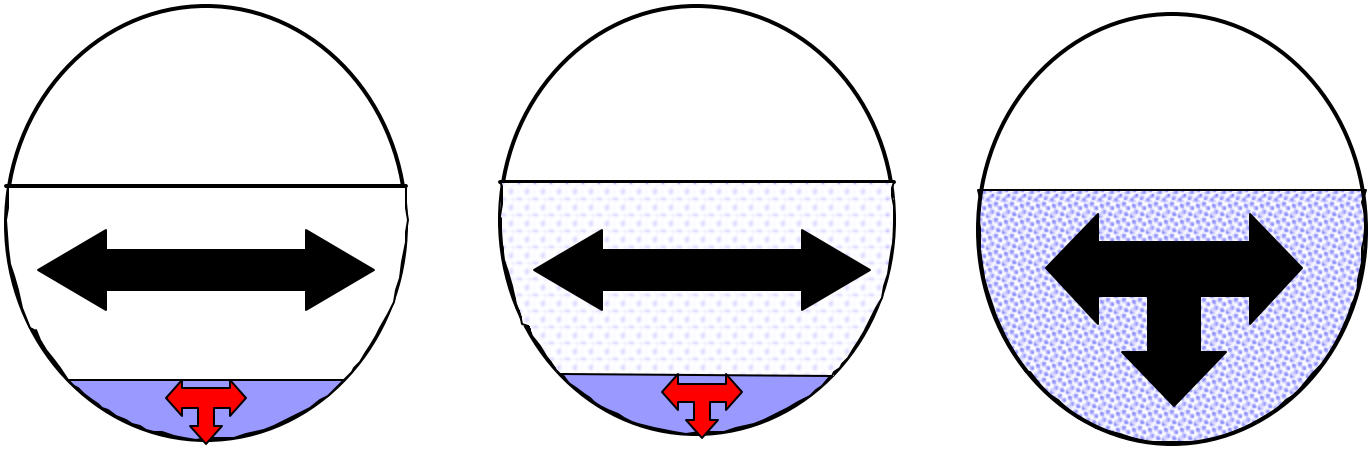
General Background

- In general biomass based fuels:
  - Can be more aggressive than petroleum based fuels,
  - Can be electrically conductive therefore corrosive,
  - Are capable of permeating non-metals,
  - Contain chemical functional groups that increase chemical activity, reactivity, and bioavailability
  - Significantly increase in biodegradability

General Background

- Material compatibility concerns with USTs include:
  - Compatibility between the product and the metallic and nonmetallic system components,
  - Compatibility between contaminants and the metallic and nonmetallic system components
  - Compatibility between the product, contaminants and in-tank equipment.

General Background



	Petroleum	Biodiesel	E10 & E85
Dissolved Water	= 100 ppm	1250 - 2500 ppm	4,000 - 40,000 ppm
Free Water	Yes	Yes	No

General Background

- General Definition for Compatibility:
  - For metals, compatibility often implies corrosion resistance.
  - For non-metals compatibility often implies resistance to a change in properties due to chemical exposure,

General Background

- 40CFR280.12 Definitions for Compatible:
  - COMPATIBLE means the ability of two or more substances to maintain their respective physical and chemical properties upon contact with one another for the design life of the tank system under conditions likely to be encountered in the UST.
  - Specification does not differentiate between product or contaminants [water].

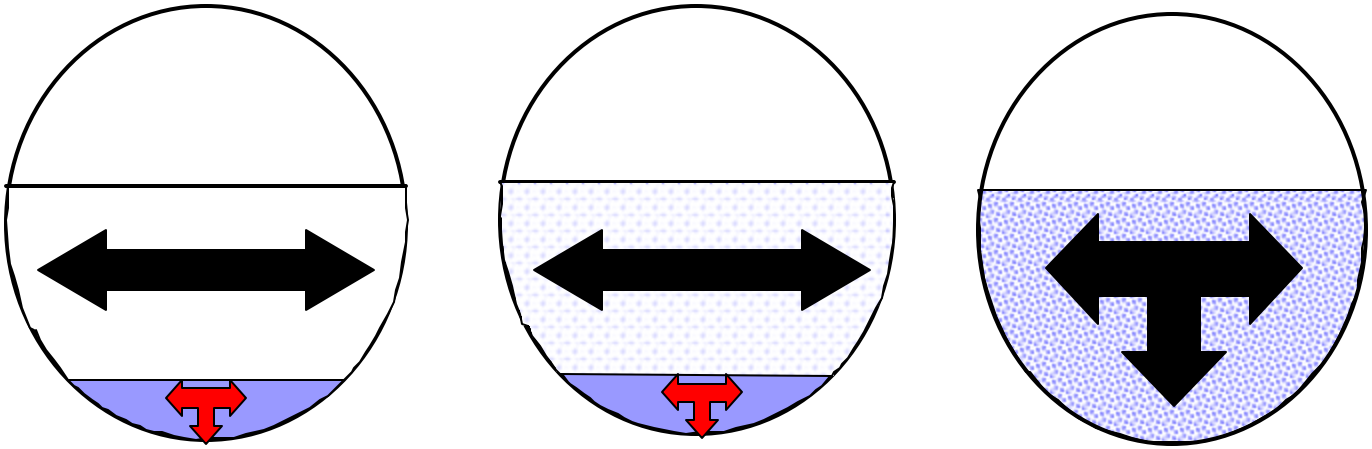
General Background

- Symptoms of material incompatibility in UST:
  - Corrosion of metallic components
    - Galvanic or pitting corrosion
    - Accelerated corrosion due to microbial activity - Microbially Influenced Corrosion (MIC),
  - Leaking, swelling, and damage to non-metallic components
  - Degradation in performance or output of internal instrumentation,

General Background

- Generally, factors that contribute to the corrosion of metals include:
  - Water & chemical contaminants
  - Microorganisms (bacteria, yeast, and mold)
  - Change in solution pH, due to acids from microbial metabolites
  - Metal alloys
  - Anodic “soft” metals that corrode under galvanic conditions

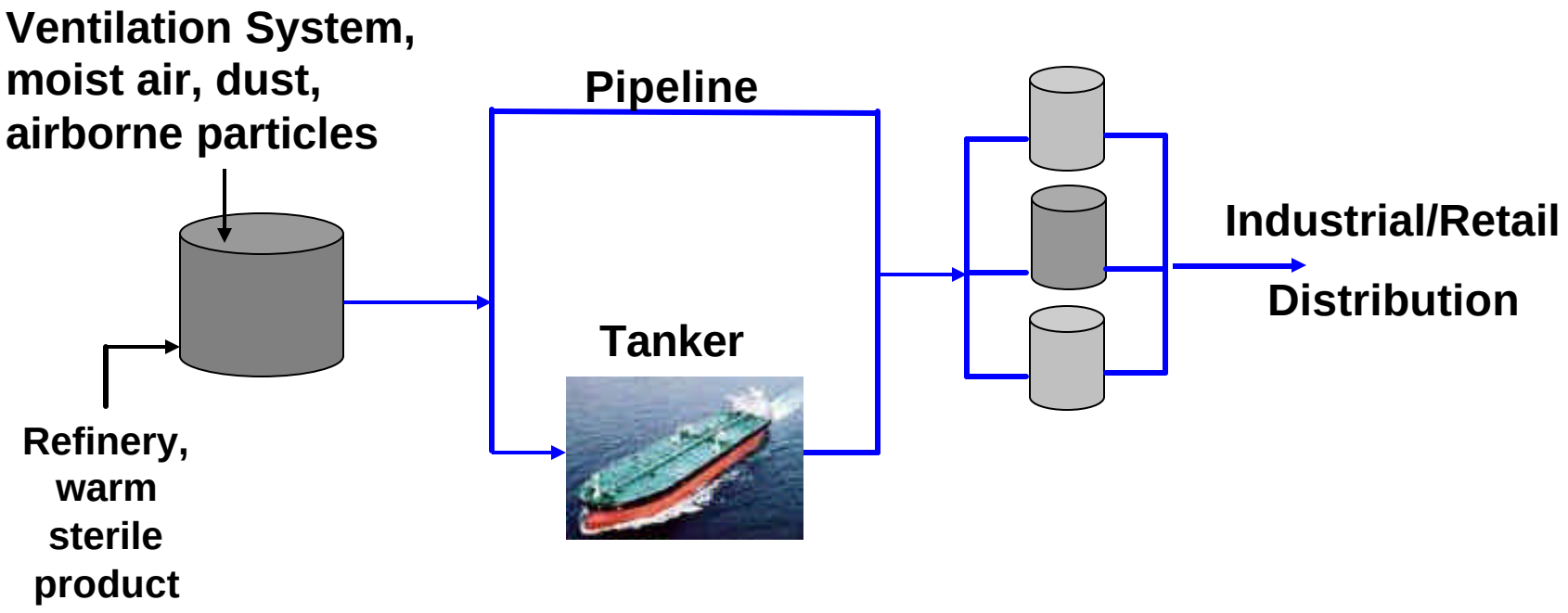
General Background



	Petroleum	Biodiesel	E10 & E85
Dissolved Water	= 100 ppm	1250 - 2500 ppm	4000 - 40,000 ppm
Free Water	Yes	Yes	No
Metal Corrosion	Below water line	Primarily below the water line	Overall system corrosion

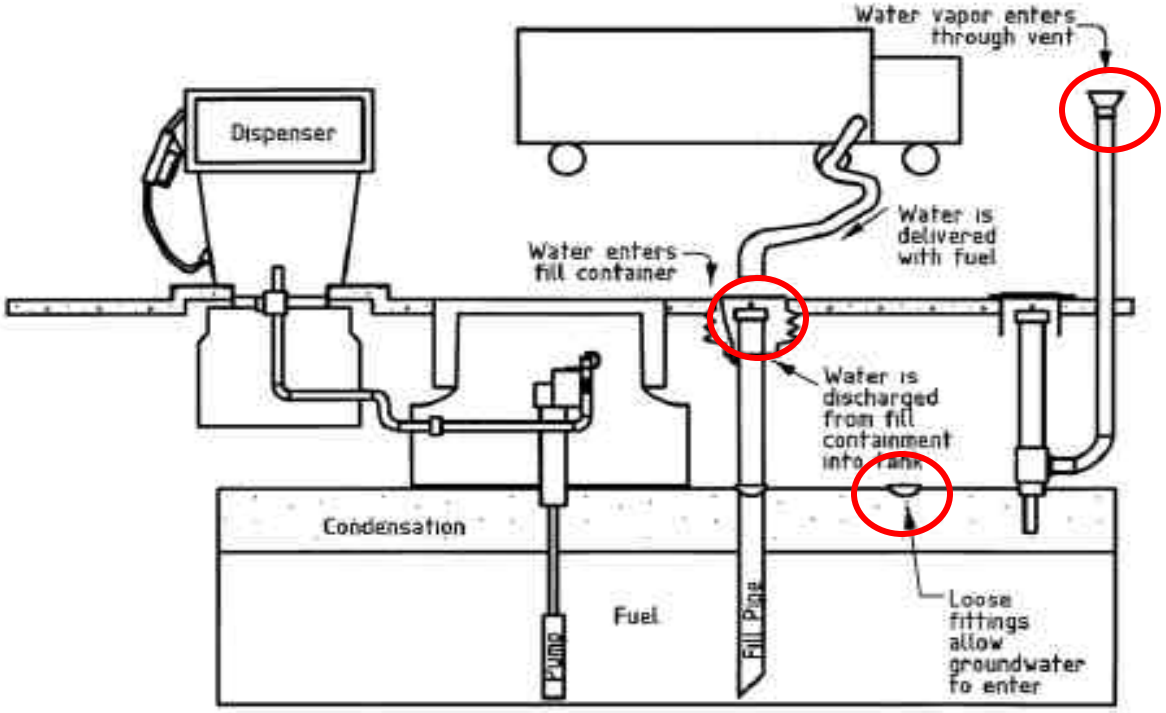
General Background

Primary Sources of Water and Contaminants



General Background

Secondary Source of Water and Contaminants

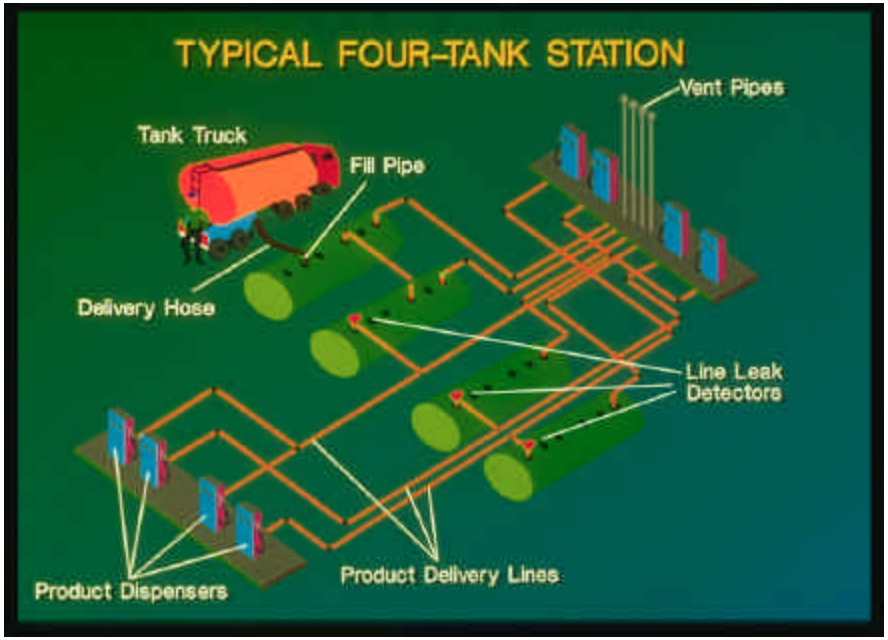


Steel Tank Institute: "Keeping Water Out of Your Storage System," March 2004

General Background

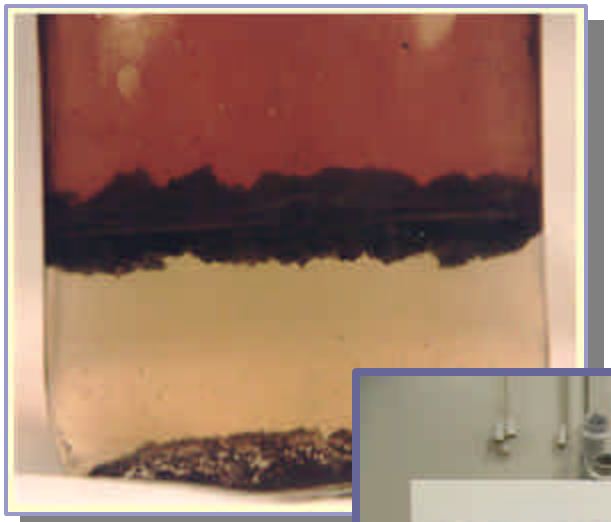
Tertiary Source of Water and Contaminants

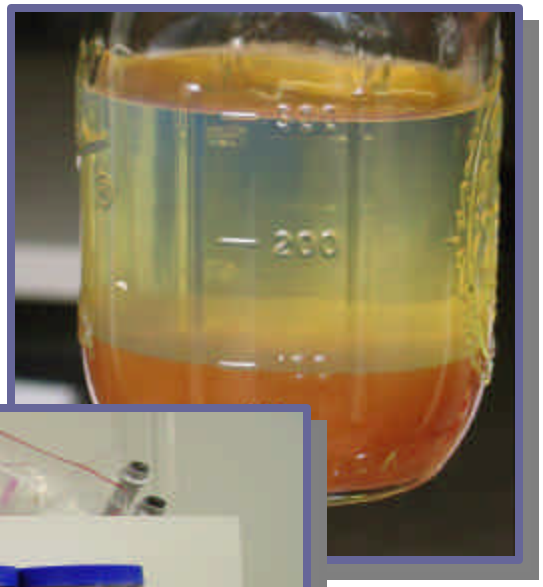
- Installation of new UST:
  - Using water to ballast UST during construction and installation,



Effects of Water in Fuels

Diesel





Gasoline

Biodiesel

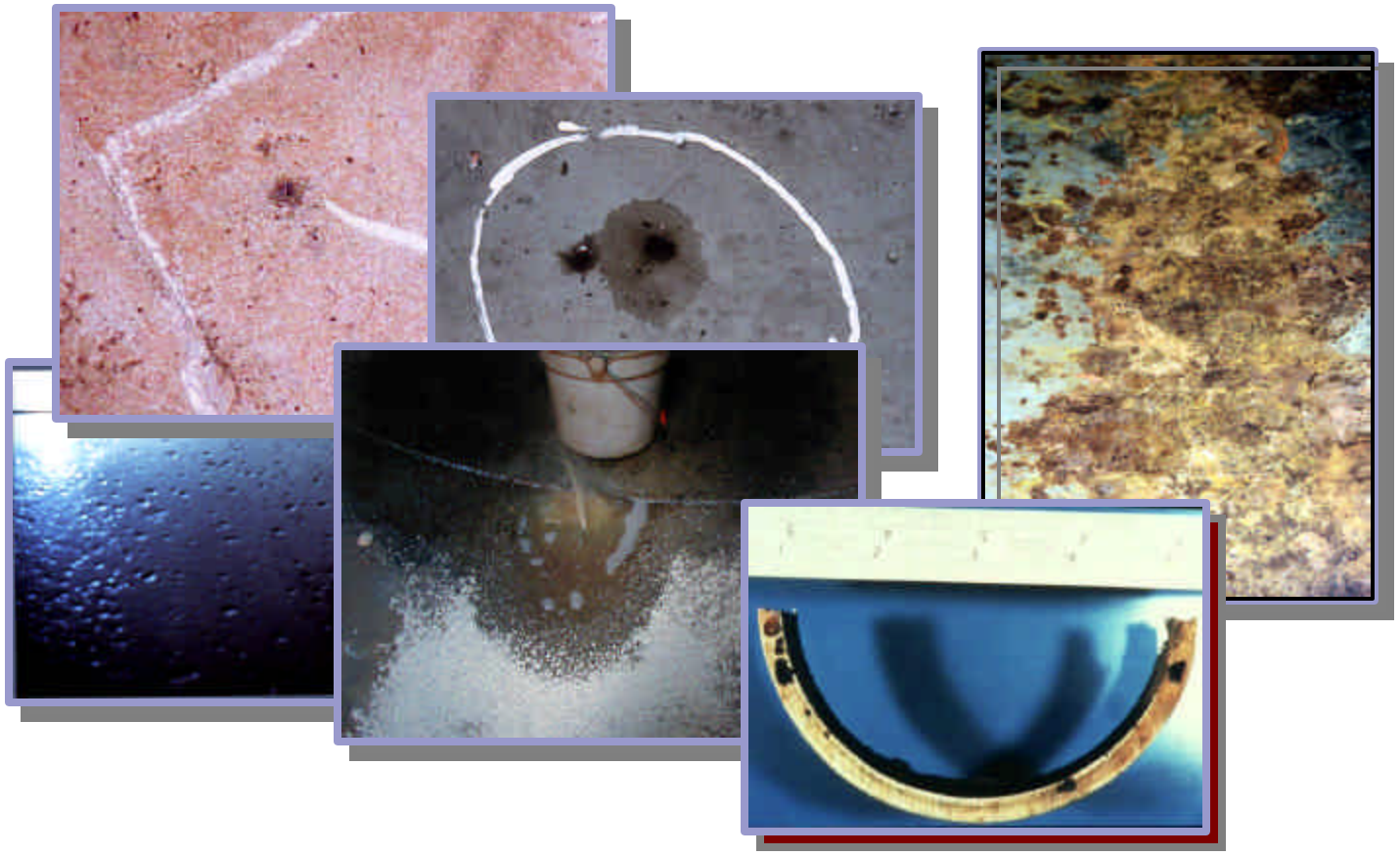
Effects of Water in a UST

Fill End

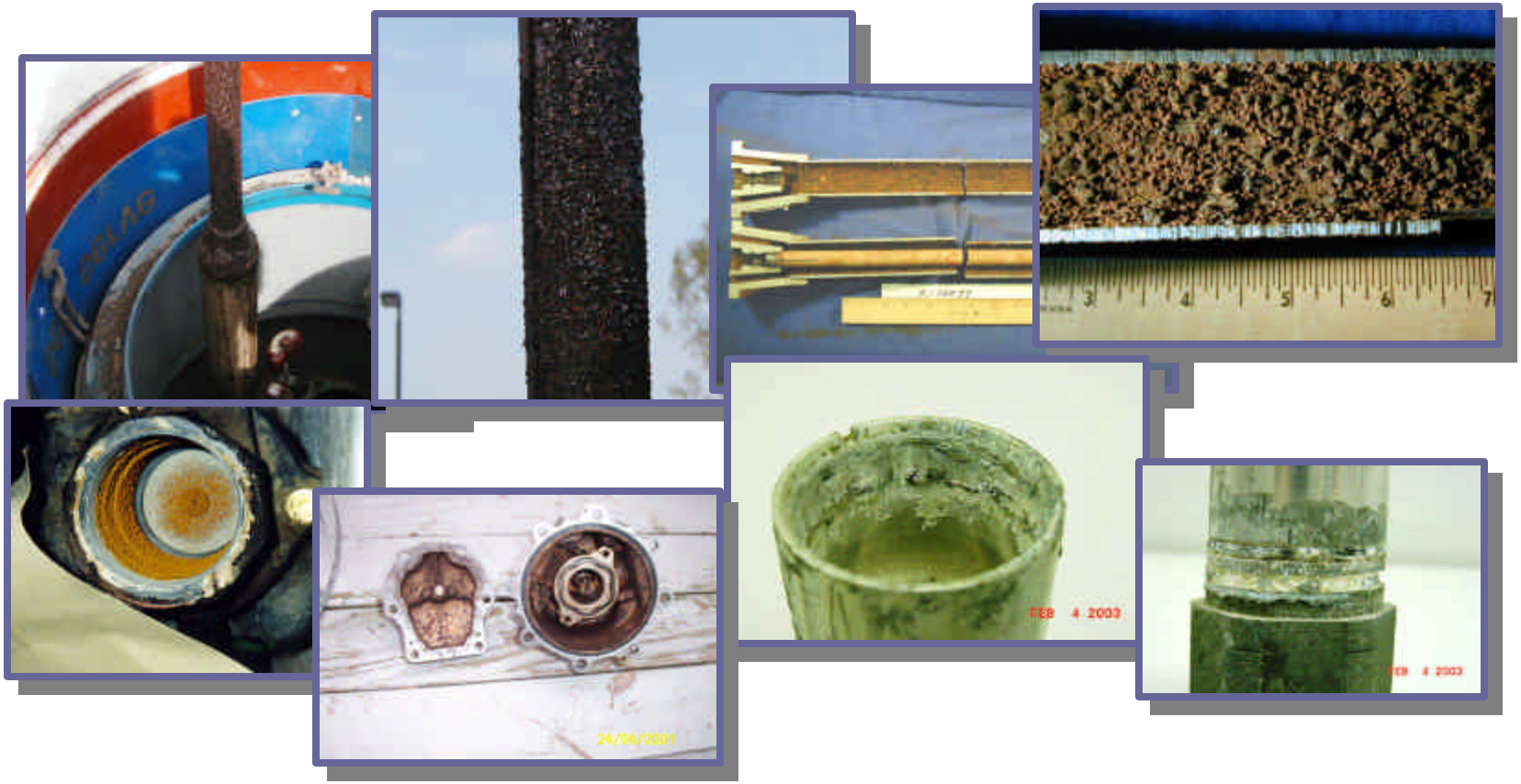
Pump End

Examples of metal corrosion

Examples of metal corrosion



Examples of metal corrosion



General Background

- Factors that contribute to degradation of non-metallic components,
  - Solvent ingress driven by some type of gradient,
  - Interaction between the solvent and elastomer or polymer matrix,
  - Loss antioxidants, fillers, heat stabilizers, plasticizers due to solvent permeation,
  - Solvent diffusion effecting strength and stiffness.

General Background

- Symptoms of material incompatibility in UST:,
  - Discoloration
  - Swelling
  - Degradation
  - Elongation/Creep
  - Softening / Jellying
  - Embrittlement
  - Delamination

General Background

- Elastomers:
  - Dynamic Applications - up to a 10-15% swell can usually be tolerated
  - Static applications - up to 30% swell in “O” ring volume can be tolerated,

Examples of non-metal degradation:

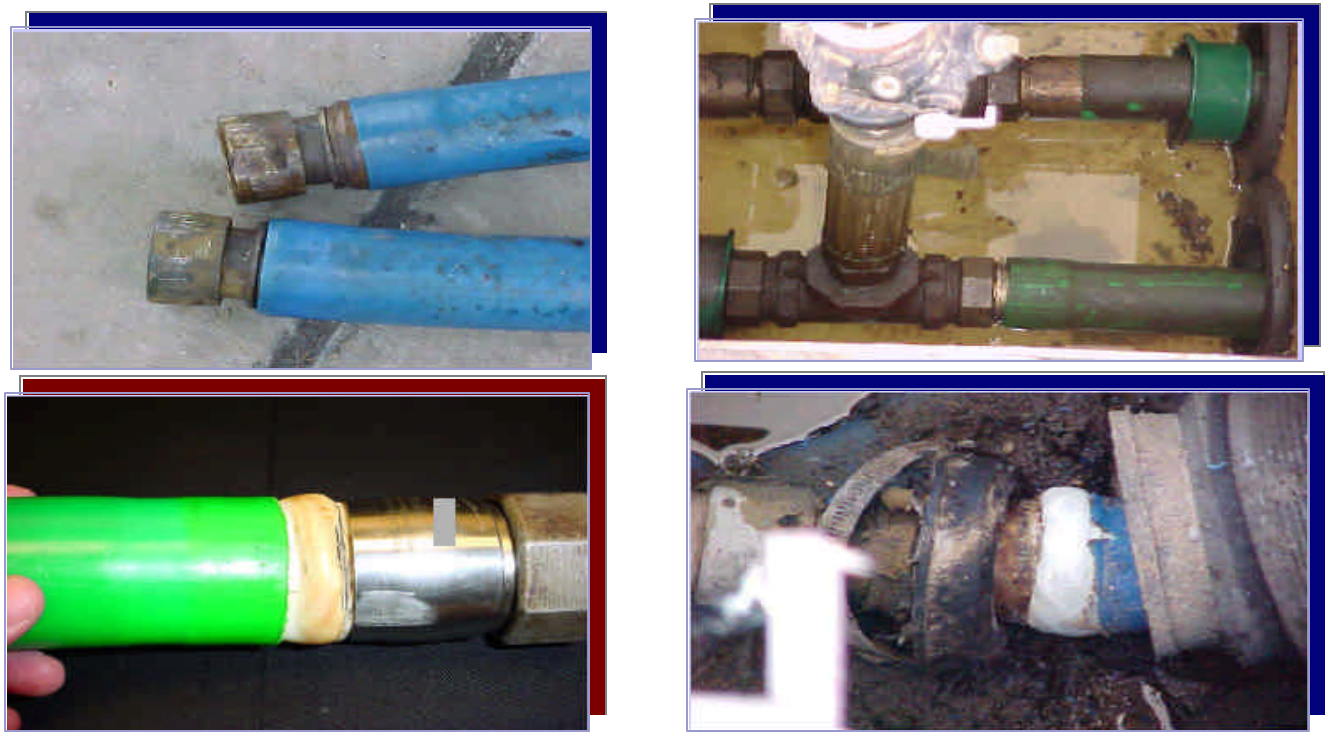
#2 Rigid FRP pipe with scratch or score on surface

#4 Internal color change of carrier portion of pipe from ivory to black; very brittle

#8 Black mold growth; degradation of single-wall pipe's external cover

Courtesy: Ernest M. Roggelin, FDEP/UST, Lustline #47

Examples of non-metal degradation:



Titled: Swelling and Bulging

Source: Mississippi Department of Environmental Quality, January 2003.

Examples of non-metal degradation:

Titled: Soft and Spongy

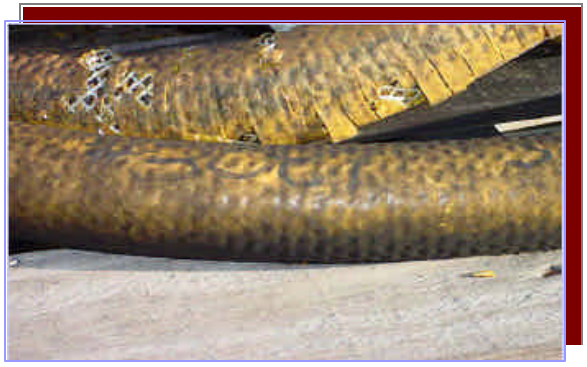
Source: Mississippi Department of Environmental Quality, January 2003.

#13 Softening of single-walled pipe with product being squeezed out

#12 Jelling of single-walled pipe

Courtesy: Ernest M. Roggelin, FDEP/UST, Lustline #47

Examples of non-metal degradation:



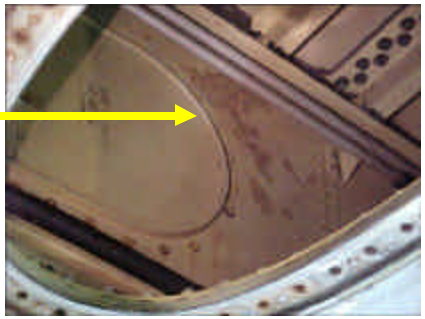
Titled: Delamination or Microbial Growth

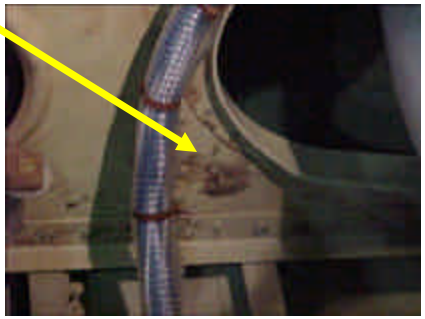
Source: Mississippi Department of Environmental Quality, January 2003.

Example of thermoset degradation:

Fiberglass Tank Section

Aircraft Wing Tank





Staining

Close Up

Spider Fracture

Example of thermoset degradation:

PETROLEUM BASED FUELS

Gasolines

Diesels

Petroleum Based Fuels

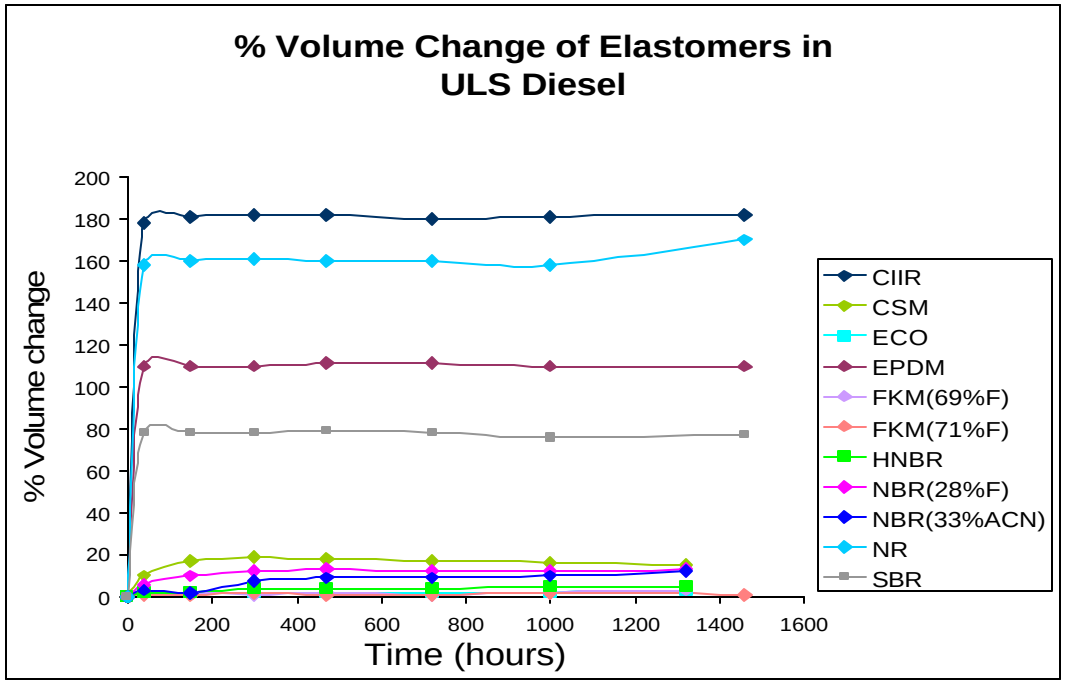
- Recommended Metals
  - No known issues with existing metals
    - aluminum,
    - carbon steel,
    - stainless steel, and
    - bronze,
- Not Recommended Metals;
  - Copper & Zinc
  - Both are oxidative catalysts that will accelerate the formation of sediment, gels and soaps (ASTM D975, Appendix X2.7.2)

Petroleum Based Fuels

- Recommended Elastomers
  - No known issues with most existing elastomers,
- Not Recommended Elastomers
  - No known issues with most existing elastomers.
  - Exceptions noted

Experimental Data ULSD Test

IASH September 2005



Elastomer type	Compound designation
Acrylonitrile-butadiene (nitrile) – 5	NBR(33% ACN)
Acrylonitrile-butadiene (nitrile) - 6	NBR(28% ACN)
Epichlorohydrin -3	ECO*
Fluorocarbon-1&2	FKM (69% F)
Fluorocarbon -1&2	FKM (71% F)
Hydrogenated nitrile-4	HNBR*
Chlorinated Isobutylene Isopropene (Chlorobutyl)	CIIR
Ethylene-propylene	EPDM
Styrene-butadiene	SBR
Natural Rubber	NR
Chlorosulphonated polyethylene -7	CSM

Courtesy of: ***Janice I. Hetherington* and Stephanie Green*****,**

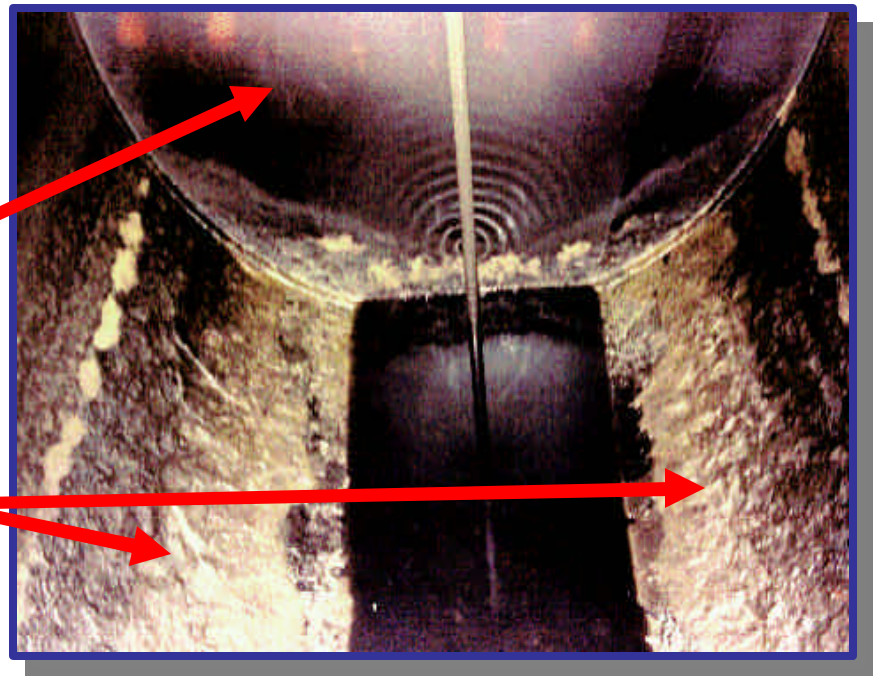
Cranfield University, Defence Academy of the United Kingdom.

Petroleum Based Fuels

- Recommended Polymers;
  - No known issues with most existing elastomers,,
- Not Recommended Polymers;
  - No known issues with most existing elastomers,

Petroleum Based Fuels

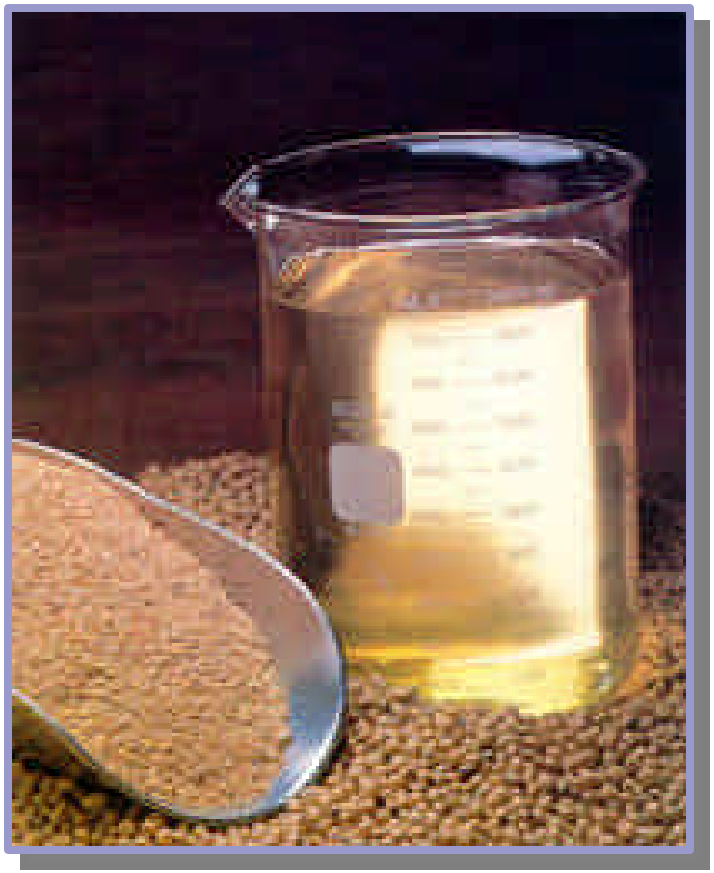
- Other Important Compatibility Issues:
  - Generally, there should be few material compatibility issues between petroleum product and currently approved system materials,
  - The presence of water will continue to promote and support MIC as well as general corrosion below the water line,



Petroleum Based Fuels

- Other Important Compatibility Issues:
  - The ubiquitous presence of water and microbes water in the petroleum distribution, storage, and distribution system assures:
    - System degradation due to MIC (microbially influenced corrosion),
    - Metal corrosion,
    - Equipment damage and,

BIODIESEL BLEND FUELS



Biodiesel

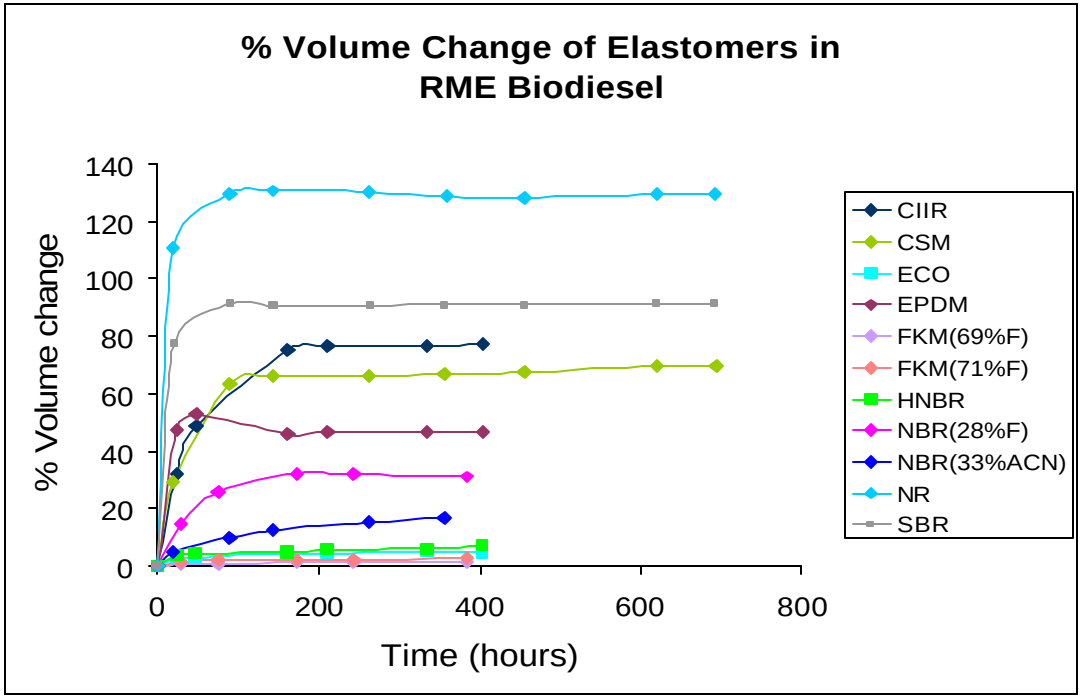
- Recommended Metals
  - Most metals found in a retail fueling facility including
    - stainless steel,
    - carbon steel, or
    - aluminum
- Not Recommended Metals;
  - brass, bronze, copper, lead, tin, and zinc will accelerate oxidation of biodiesel and create insoluble sediment or gels and salts.
  - Lead solders, zinc linings, copper pipes, brass regulators and copper fittings should be avoided,

Biodiesel

Elastomers	Blend	Compared to Diesel
PTFE - Teflon®	B100	Little Change
Polyamide - Nylon 6/6 ®	B100	Little Change
Fluorocarbon Viton A401-C & GFLT ®	B100	Little Change
Nitrile	B100	Hardness ? - 20% : Swell ? - 18%
Fluorosilicone	B100	Hardness Neg. : Swell ? - 7%
Polyurethane	B100	Hardness Neg. : Swell ? - 6%
Polypropylene	B100	Hardness ? - 10% : Swell ? - 8-15%
Polyvinyl	B100-B30	Worse
Polyvinyl	B20 – B10	Comparable
Polyvinylchloride - Tygon®	B100	Worse

Biodiesel

IASH September 2005



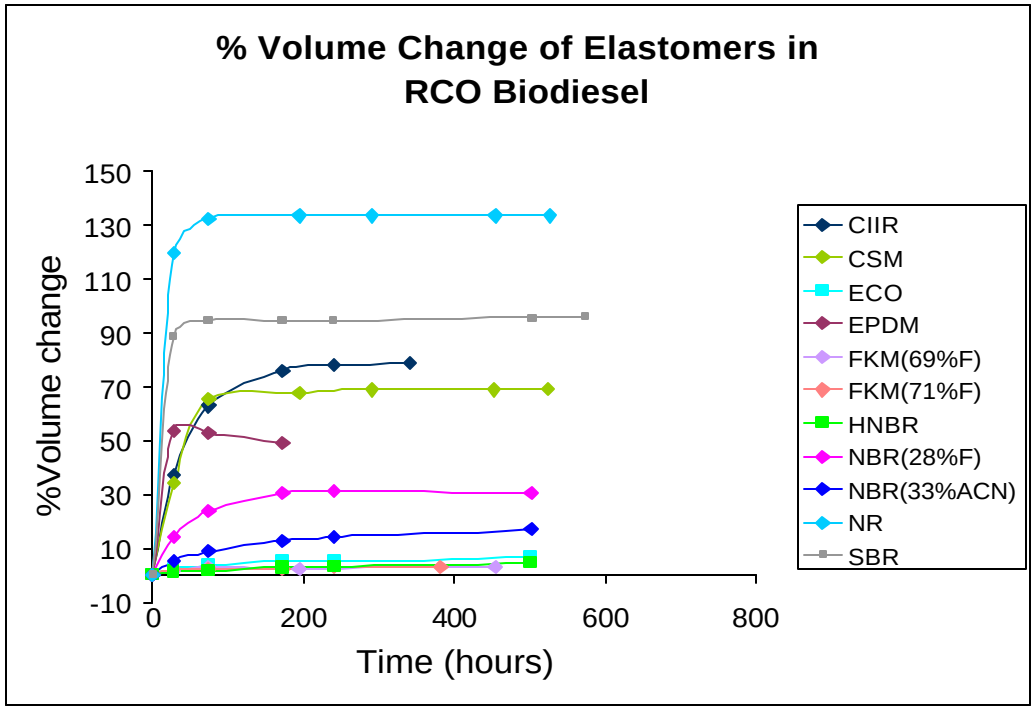
Elastomer type	Compound designation
Acrylonitrile-butadiene (nitrile)-6	NBR(33% ACN)
Acrylonitrile-butadiene (nitrile)-5	NBR(28% ACN)
Epichlorohydrin-3	ECO
Fluorocarbon-2	FKM (69% F)
Fluorocarbon-1	FKM (71% F)
Hydrogenated nitrile-4	HNBR
Chlorinated Isobutylene Isopropene (Chlorobutyl)	CIIR
Ethylene-propylene	EPDM
Styrene-butadiene	SBR
Natural Rubber	NR
Chlorosulphonated polyethylene	CSM

Courtesy of: *Janice I. Hetherington* and Stephanie Green*,

Cranfield University, Defence Academy of the United Kingdom.

Biodiesel

IASH September 2005



Courtesy of: *Janice I. Hetherington* and Stephanie Green*, Cranfield University, Defence Academy of the United Kingdom.

Elastomer type	Compound designation
Acrylonitrile-butadiene (nitrile)-5	NBR(33% ACN)
Acrylonitrile-butadiene (nitrile)-6	NBR(28% ACN)
Epichlorohydrin-4	ECO
Fluorocarbon-1&2	FKM (69% F)
Fluorocarbon-1&2	FKM (71% F)
Hydrogenated nitrile-3	HNBR
Chlorinated Isobutylene Isopropene (Chlorobutyl)	CIIR
Ethylene-propylene	EPDM
Styrene-butadiene	SBR
Natural Rubber	NR
Chlorosulphonated polyethylene	CSM

Biodiesel

- Compatible Polymers;
  - Polyamide
  - Polyethylene
  - Polypropylene
  - Acryl & Epoxy (paints)
- Incompatible Polymers:
  - Hypalon (chlorosulfonated polyethylene)
  - Polyurethanes

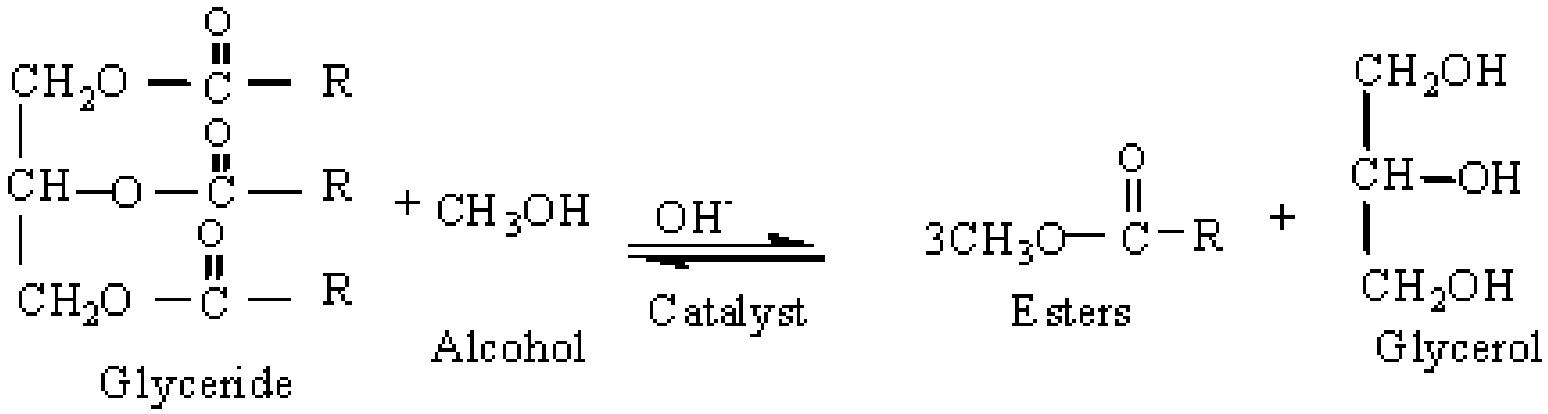
Biodiesel

- Vegetable Oil Production
  (Billions pounds/year)
  - Soybean 18.340*
  - Corn 2.420
  - Cottonseed 1.010
  - Sunflower 1.000
  - Peanuts 0.220
  - Others 0.669
    - Total 23.659

- Animal Fats
  (Billions pounds/year)
  - Inedible Tallow 3.859
  - Yellow Grease 2.633
  - Poultry Fat 2.215
  - Edible Tallow 1.625
  - Lard & Greases 1.306
    - Total 11.638

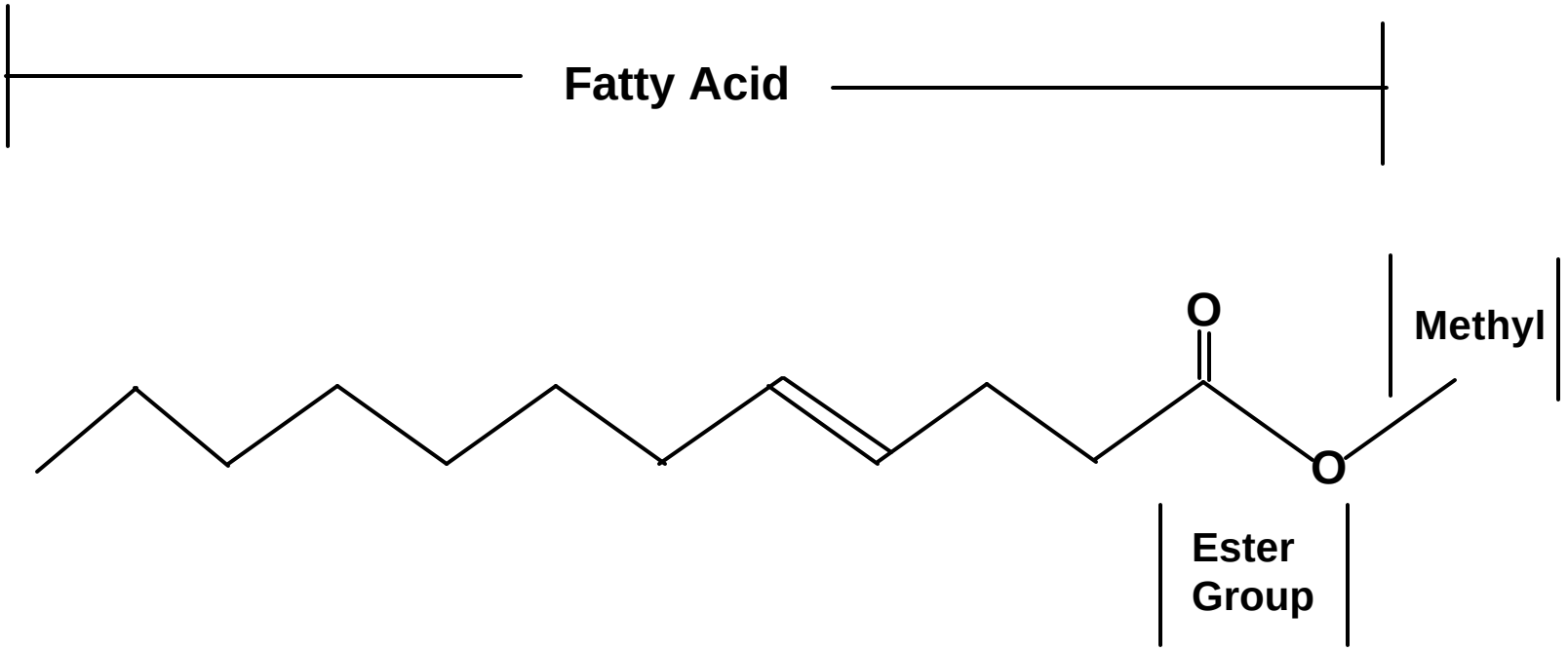
Biodiesel

- Manufacturing Process



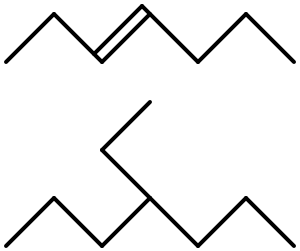
Biodiesel

- Simple Structure – Fatty Acid Methyl Ester:

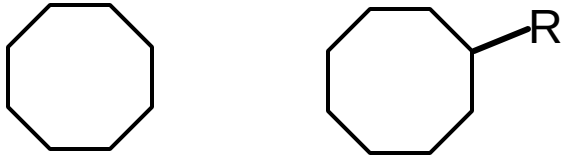


Biodiesel / Diesel Comparison

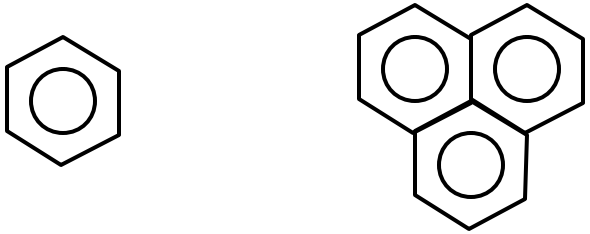
- Simple Structures In Petroleum Fuels:
  - Linear & branched hydrocarbons



  - Cyclic

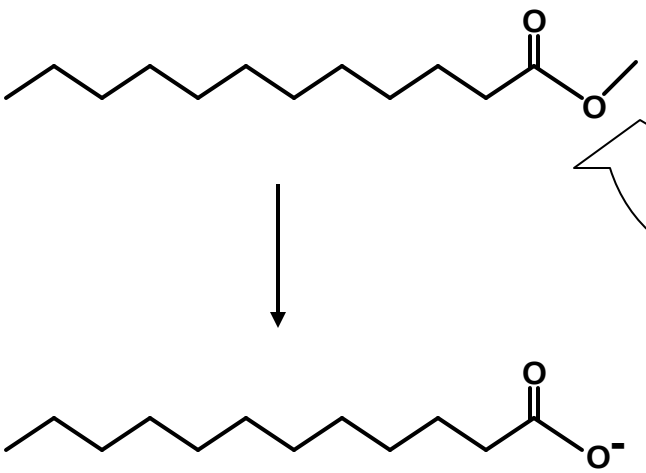


  - Aromatic & Polyaromatic



Biodiesel / Biodeterioration

- Mono alkyl ester fatty acid:



Enzymatic attack of

the terminal methyl group

Fatty Acid **+** **free methyl group**

(Solubility proportional to carbon length)

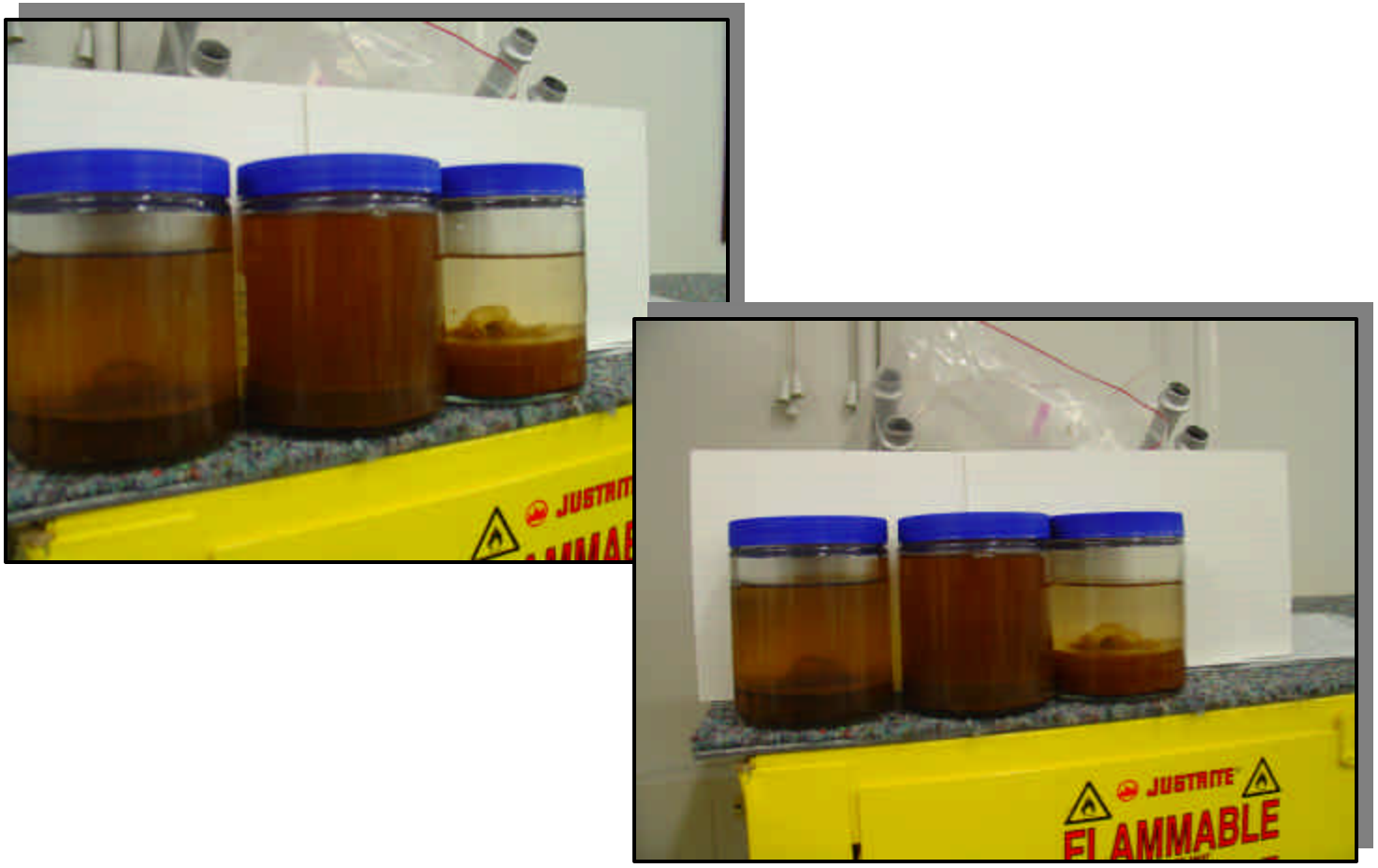
Biodiesel

- Potential Issues and Concerns (B100):
  - B100 is a strong solvent and will release varnish and gums from diesel fuel tank walls and piping into the bulk fuel plugging in-line filters,
  - Biodiesel is hygroscopic and can hold between 1200 – 2500 ppm water,
  - Biodiesel not meeting ASTM D6751 can damage equipment and plug filters, (i.e., Minnesota B2 issue)

Biodiesel

- Other Potential Issues and Concerns:
  - Aerobically, biodiesel will biodegrade in seven (7) days
  - Anaerobically, biodiesel will biodegrade in 14 days,
  - Biodiesel has a very favorable biodegradation profile
    - B100 can biodegrade 4 times faster than petroleum diesel
    - B20 can biodegrade twice as fast as petroleum diesel,

Biodiesel



Biodiesel

- Potential Issues and Concerns (General):
  - Aged biodiesel can form aggressive acids that result in further damage,
  - The water-fuel interface can be very corrosive to the UST systems components and can also promote microbial growth,
  - Biodiesel has been used successfully to biostimulate and bioremediate crude oil spills

ETHANOL BLEND FUELS

E85
85% Ethanol
CLEAN DOMESTIC RENEWABLE

Ethanol Blends – E10

- Recommended Metals
  - E-blend fuels = 10% do not pose a materials compatibility issue for metals including:
    - aluminum,
    - carbon steel,
    - stainless steel, and
    - bronze,
- Not Recommended Metals;
  - Zinc-galvanized is not recommended for E10 blends

Ethanol Blends – E85

- Recommended Metals;
  - Stainless steel (Best)
  - Mild steel
  - Unplated steel
  - Black Iron
  - Bronze
  - Nickel Plated

    (for soft metals such as aluminum or brass fittings)
- Not Recommended Metals;
  - Aluminum
  - Brass
  - Copper Alloys
  - Lead
  - Lead Solder
  - Tern-plated steel
  - Zinc

Ethanol Blends – E10

- Recommended Elastomers
  - Fluorocarbons
  - Fluorosilicone,
  - Buna-N (hoses & gaskets),
  - Natural rubber
  - Polychloroprene (hoses & gaskets),
  - Polysulfide rubber
- Not Recommended Elastomers
  - Buna-N (seals),
  - Polychloroprene (seals),
  - Urethane rubber

Ethanol Blends – E85

- Recommended Elastomers
  - Fluorocarbon
  - Buna-N,
  - Nitrile Rubbers
  - Polychloroprene
  - Polytetrafluoroethylene
- Not Recommended Elastomers
  - Natural rubber
  - Cork gasket material,
  - Leather,

Ethanol Blends – E10

- Recommended Polymers;
  - Acetal
  - Polyamides
  - Polypropylene
  - Polytetrafluoroethylene
  - Fiberglass reinforced plastic
- Not Recommended Polymers;
  - Polyurethane
  - Alcohol-based pipe dope

Ethanol Blends – E85

- Recommended Elastomers
  - Polypropylene
  - Thermoset reinforced fiberglass
  - Thermoplastic piping,
  - UL Listed fiberglass tanks,
- Not Recommended Elastomers
  - Polyurethane,
  - PVC,
  - polyamides,
  - methyl-methacrylate plastics,
  - Certain thermoplastics and thermoset resins*

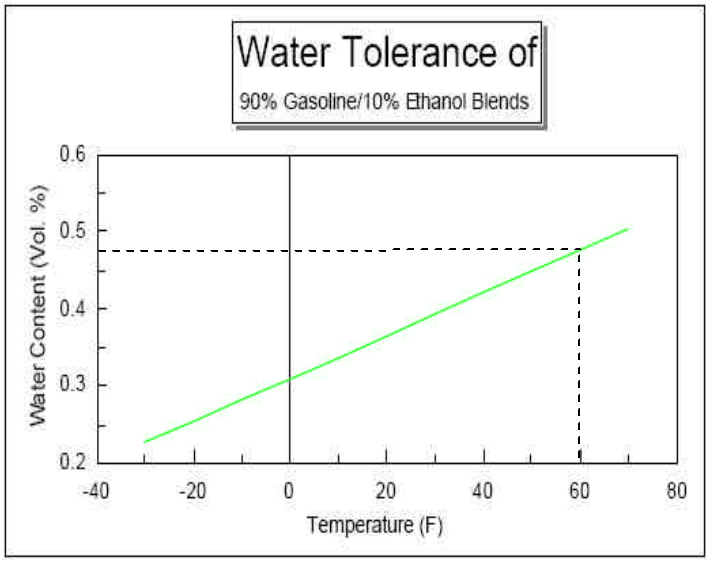
***epoxies and polyester resins manufactured between 1970's and 1980's**

Ethanol Blends

- Potential Issues and Concerns,
  - Phase Separation
  - Fuel Conductivity/Corrosion
  - Solvent Action
  - Compatibility and Permeability

Ethanol Blends

- Phase Separation:
  - Water not soluble in gasoline,
  - EtOH and water are infinitely soluble in each other
  - Gasoline can hold ~ 0.19%,
  - E10 can hold ~ 0.49%,
  - Water/Ethanol will phase separate once fuel is water saturated,
  - Water absorption is why EtOH and E10 blends cannot be shipped via pipeline,



Ethanol Blends

- Fuel conductivity / Corrosion
  - Gasoline is benign and nonconductive,
  - EtOH has greater conductive (10^{-9} mho/cm)
  - Water & chemical contaminants are soluble in EtOH and will increase overall conductivity of EtOH blended fuels,
  - Water saturated E10 may experience wet corrosion, galvanic, or electrolytic corrosion,

Ethanol Blends

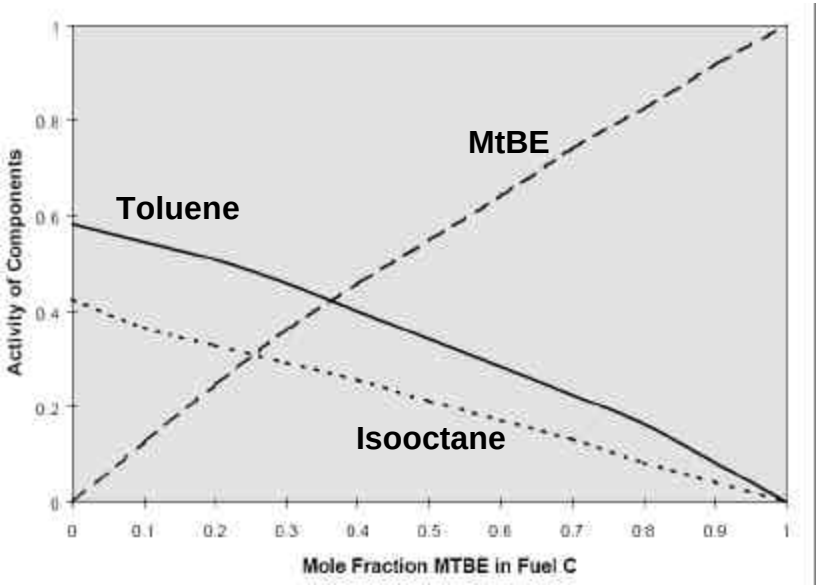
- Solvent Action
  - Fuel blended with EtOH can loosen rust and concretions from interior walls of tanks and suspend sediment,
- Compatibility/Permeability:
  - Potential compatibility issues between ethanol blended fuels and system metals and non-metals, due to the solution conductivity and activity of the alcohol,

Ethanol Blends

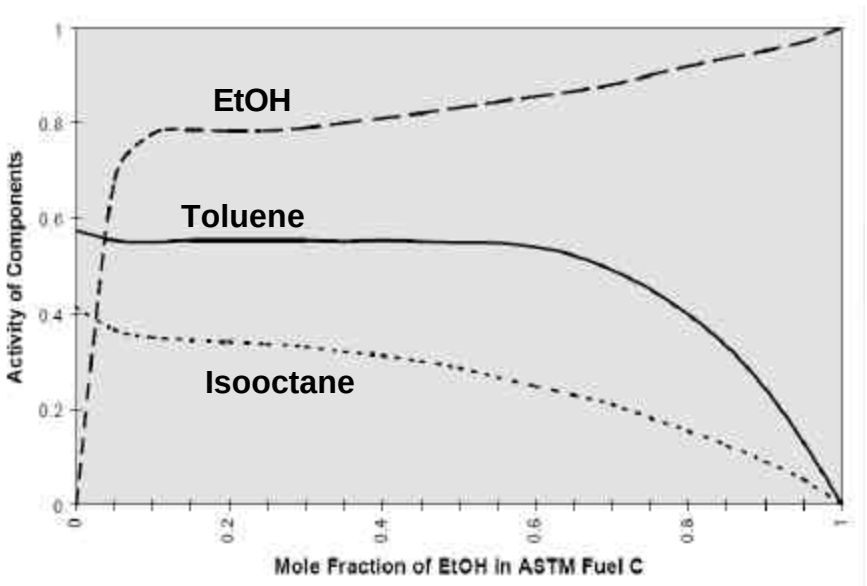
- Factors that contribute to degradation of non-metallic components,
  - Permeation (solvent ingress driven by chemical activity gradient)
  - Swelling (interaction between the solvent, elastomer or polymer),
  - Plasticizer Extraction
    - Loss or migration of antioxidants, heat stabilizers, plasticizers out of a elastomers and flexible thermoplastics by the solvent),
  - Deplasticization (solvent diffusion effecting strength and stiffness)

Ethanol Blends

Activity of MtBE, Toluene, and Isooctane as a function of ether in ASTM Fuel C

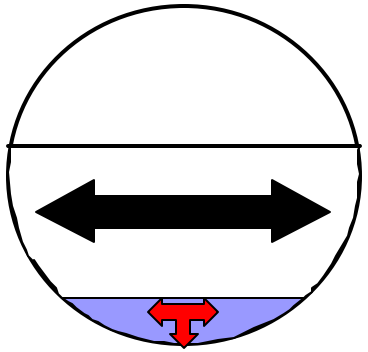


Activity of EtOH, Toluene, and Isooctane as a function of ether in ASTM Fuel C



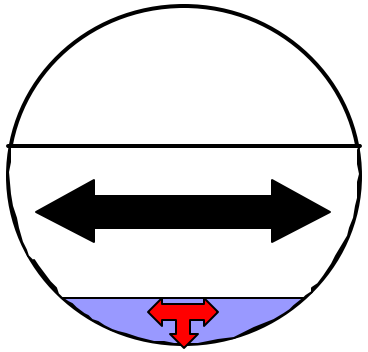
Conclusion

Petroleum Based Fuels



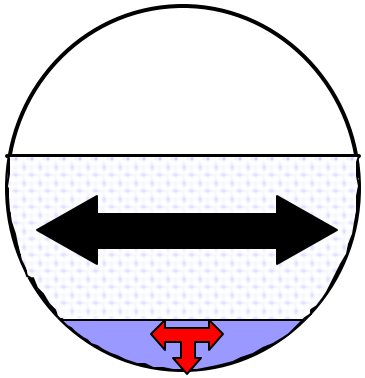
- Summary:
  - In theory, material compatibility issues between petroleum based fuels and currently approved system materials should be minimal,
  - Water is generally present in the fuel storage, distribution, and dispensing system.
  - Water supports a variety of corrosion processes including galvanic corrosion and pitting corrosion,

Petroleum Based Fuels



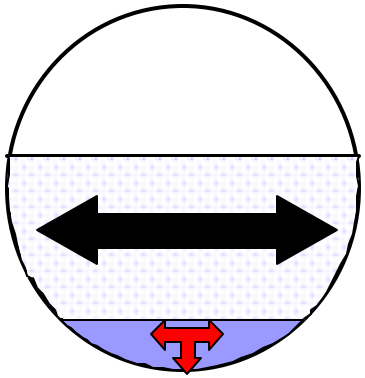
- Summary:
  - The presence of water supports microbial growth which accelerates metal corrosion, equipment damage and contributes to equipment performance degradation due to the presence of MIC,
  - Current corrosion mitigation methods only target external corrosion processes,
  - Internal corrosion due to the presence of water and MIC are not mitigated or cured using current corrosion mitigation tools such as cathodic protection.

Biodiesel



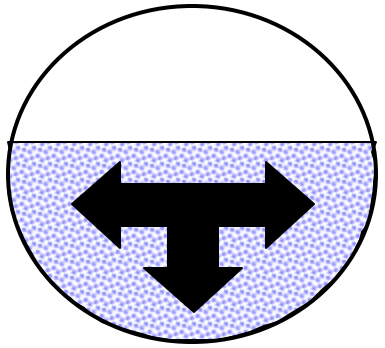
- Potential Issues and Concerns (B100):
  - B100 is a strong solvent and will release varnish and gums tank walls and piping into the bulk fuel plugging in-line filters,
  - Biodiesel not meeting ASTM D6751 can damage equipment and plug filters, (i.e., Minnesota B2 issue)
  - Aged biodiesel can form aggressive acids that result in further system corrosion,
  - Cold temperatures or cold temperature spikes will cause certain biodiesel to gel.

Biodiesel



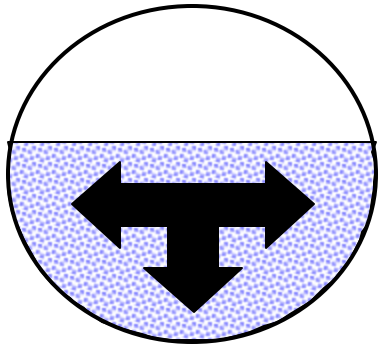
- Summary
  - Biodegradability of biodiesel makes it a excellent candidate for use in environmentally sensitive areas,
  - However, the presence of water supports microbial growth which accelerates metal corrosion, equipment damage and equipment malfunction due to the presence of MIC.
  - Current corrosion mitigation methods only target external corrosion processes
  - Internal corrosion due to the presence of water and MIC are not mitigated or cured using current corrosion mitigation tools such as cathodic protection.

Ethanol Blends – E10



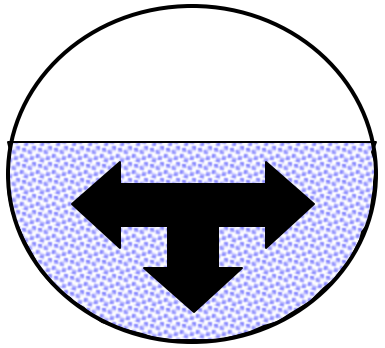
- Summary
  - E10 blends have been in use for nearly three decades,
  - Most, if not all, material compatibility issues have been identified and resolved,
  - For fuel system conversions, thoroughly clean, dewater, and inspect tanks before placing into service,
  - Use materials that are approved for use with ethanol (i.e., state approved or UL approved),

Ethanol Blends – E10



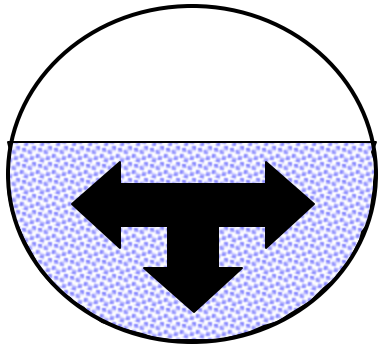
- Summary
  - Housekeeping and an active surveillance program are still needed to minimize the effects of water and aqueous contaminants that contribute to:
    - Corrosion mechanisms of metals,
    - Microbial growth (E10 only),
    - Degradation of elastomers, thermoplastics, and possibly thermosets,
    - Potential degradation of internal instrumentation readout.

Ethanol Blends – E85



- Summary
  - For fuel conversion, always use an experienced, licensed and bonded installer to clean and install E85 tanks,
  - E85 fuel could be contaminated during blending, transportation, storage, and dispensing,
  - Install and use properly sized in-line filters on the dispensers, (e.g., particle size and efficiency),
  - Vehicles can experience problems weeks or months after site installation or conversion,

Ethanol Blends – E85



- Summary
  - Consult with State and Local agencies regarding installation or conversion guidelines or requirements,
  - Use only E85 compatible equipment or equipment approved by UL,
  - Ethanol content for E85 is at a sufficient level to prevent microbial influenced corrosion.

Total Fuel Quality

totalfuelquality.com

www.totalfuelquality.com

Fuel Quality Services, Inc.

"Where Quality is Our Number One Service"

Kathon® FP 1.5

An Industrial Microbiocide For Use As A Fuel Preservative

www.fqsinc.com

Edward W, English, II – Vice President and Technical Director, – Fuel Quality Services, Inc.
P.O. Box 1380 – Flowery Branch, GA. 30542
(770) 967-9790 – email: eenglish@fqsinc.com

Jim Hansen – President, Downstream – Fuel Quality Services, Inc.
309 Mohawk Drive – Rotterdam Junction, NY 12150
518-424-3162 cell – 518-887-3024 office – 518-887-3125 fax